Lawrence Berkeley National Laboratory

Recent Work

Title

Extracting Natural Biosurfactants from Humus Deposits for Subsurface Engineering Applications

Permalink

<https://escholarship.org/uc/item/3z79x6xq>

Journal

Energy and Fuels, 31(11)

ISSN

0887-0624

Authors

Wan, J
Tokunaga, TK
Dong, W
[et al.](#)

Publication Date

2017-11-16

DOI

10.1021/acs.energyfuels.7b02203

Peer reviewed

Extracting Natural Biosurfactants from Humus Deposits for Subsurface Engineering Applications

Jiamin Wan*, Wenming Dong, Yongman Kim, and Tetsu K. Tokunaga
Energy Geosciences Division, Earth and Environment Sciences Area,
Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley,
California 94720

Corresponding author: Jiamin Wan, 510-486-6004, jwan@lbl.gov

Keywords: natural biosurfactants, foams, viscosity, EOR, non-water
fracturing

TOC Art:

Supporting Information: video on scCO₂-foam flow

19Abstract

20More environmentally benign, economical, and effective surfactants
21and additives are increasingly needed in engineering subsurface
22energy recovery processes. Biosurfactants have some advantageous
23over chemically synthesized surfactants, however the high costs of
24microbial-biosynthesis prohibits their applications in subsurface
25engineering. Here we propose to use already naturally formed
26biosurfactants contained within Earth's abundant humus deposits for
27subsurface engineering applications. Humus is plentiful, inexpensive,
28and readily available. We collected humus samples of different types
29from four different geographic regions, and developed a simple
30method for extracting natural biosurfactant (NBS) used only four
31common chemicals. The average NBS extraction yields are 17 ± 6 % of
32the raw humus tested. No significant differences in elemental
33composition and functional group chemistry were found among the
34NBS extracted from humus of different origins, suggesting that mostly
35any humus deposits can be used as the raw material for NBS.
36Measurements of interfacial tensions between air-water and
37supercritical (sc) CO₂-water interfaces indicate that the NBS is a highly
38effective surfactant. NBS has good foaming ability. In our preliminary
39tests with only 0.5 mass % NBS in the aqueous phase (no other
40additives), the NBS generated scCO₂-in-water foams reached 90%
41foam quality with the foam apparent viscosities up to 30 cP. These
42results suggest that NBS merits further research and development as a
43potential new technology for industrial scale subsurface energy
44production.

45

46INTRODUCTION

47Using alternative fluids (e. g., CO₂, N₂, and natural gas) to replace
48water in hydraulic fracturing has become an attractive next step to

49 resolve the issues resulted from using water-based fracturing fluids,
50 including wastewater generation and treatment, and water formation
51 damage from water blocking of shale pores¹. The primary barrier of
52 using these alternative fluids is their very low viscosity, much lower
53 than that of water. Yet CO₂ has the advantage of miscibility with oil
54 under elevated pressure, and this has been driving the technology of
55 CO₂ enhanced oil recovery (EOR). However the low viscosity of CO₂
56 causes the injected CO₂ bypass the remaining oil². The thickeners for
57 directly thickening CO₂ have been developed and tested in
58 laboratories, yet the associated issues of high costs and toxicity
59 prevent their field application²⁻³. The use of surfactant-stabilized CO₂
60 foams/emulsions is more promising for CO₂ mobility control in EOR⁴.
61 Droplets of scCO₂ separated by surfactant-stabilized lamella exhibit
62 significantly increased effective viscosity. Advancements on improved
63 foam quality and viscosity have been made in the recent years with
64 newly designed surfactants and some with nanoparticles as
65 stabilizers⁵. In hydraulic fracturing, although liquid (L) CO₂, LN₂, and
66 liquid hydrocarbons have been tested and applied in the field as
67 fracturing fluids, the results suggested that higher viscosity is needed
68 for a fracturing fluid to initiate and propagate high quality fracture
69 networks, and to transport and place proppants into the fractures¹.
70 Some oil-in-water emulsions and gas-in-water foams have been
71 developed to obtain desired viscosities, but their efficiency, costs, and
72 environmental concerns associated with surfactants for generating
73 optimal properties remain key challenges.

74 Biosurfactants have been synthesized for applications in such as
75 cosmetic and pharmaceutical industries⁶. The high costs associated
76 with biosynthesizing and downstream purification prohibits their use in
77 large-scale subsurface engineering applications. Organic-rich soils and
78 sediments are common, and some of these deposits (e.g., peat,
79 leonardite) are sufficiently concentrated that they are mined and

80 marketed as soil amendments (<http://minerals.usgs.gov/minerals>).
81 Importantly, many components in natural organic materials common in
82 soils and organic-rich sediments possess both hydrophilic and
83 hydrophobic moieties⁷, hence can readily accumulate at interfaces.
84 Humus is regarded as a refractory fraction of soil organic matter, a
85 mixture of highly heterogeneous and complex polymers, created by
86 microorganisms through degradation of plants, microbes and animal
87 remains. Humus plays essential roles in benefiting soil fertility and
88 structure, and has been studied extensively due to its importance in
89 agriculture, soil chemistry, microbial ecology, and environmental
90 sciences⁷. Methods for fractionating humic substances are well
91 developed, although rather generic because of the highly complex
92 structure and aggregation into supramolecular associations^{8,9}. A large
93 fraction of humic acid is lipid-like, including characteristics of fats,
94 waxes, sterols, glycerides, and phospholipids. The micelle-like behavior
95 of humic acids in solutions reflects their amphiphilic/surfactant
96 properties¹⁰. This paper reports on our exploration of humic substances
97 as a source for natural biosurfactants (NBS) useful for stabilizing
98 emulsions and foams for potential subsurface engineering applications.
99 Extraction and characterization of NBS will be described, followed by
100 results of interfacial tension (IFT) measurements on NBS solution-air
101 and NBS solution-scCO₂ interfaces, and initial measurements of
102 effective viscosities of NBS-stabilized scCO₂ foams.

103

104 **EXPERIMENTAL**

105 **Raw materials for NBS extraction.** The raw materials from which
106 NBS was extracted included natural humus, peat and Leonardite from
107 four different sources (Figure 1): North Dakota Leonardite (Leonardite
108 Products, LLC, Williston, ND), Florida Peat (Organic Products Co.
109 Orlando, FL), Aldrich Leonardite (Cat. # H16752,
110 <http://www.sigmaaldrich.com>, from a deposit in Germany), and humic

111material extracted from peat (International Humic Substances Society,
112Pahokee Peat from Florida, Cat. # 2BS103P, [http://humic-](http://humic-substances.org)
113substances.org). The samples were used as received (< 2.0 mm). Four
114chemicals were used in NBS extraction: sodium hydroxide, hydrochloric
115acid, benzene, and methanol. These chemicals were all Reagent grade,
116but Technical/Industrial grade chemicals are expected to be suitable.

117

118**NBS extraction.** The humus samples (< 2 mm, as received) were
119oven-dried at 75 °C for 24 hours. A Soxhlet extraction was applied to
120the samples because it efficiently recycles small amounts of solvent to
121dissolve a larger amounts of substrate¹¹. We used a simple three step
122method (modified from Chilom et al.^{9b}) that involved: pretreatment,
123solvent-extraction, and alkaline-cleaning. In Step 1, we compared
124alkaline- and acid- pretreatments against no pretreatment. In alkaline-
125pretreatment 0.3 M NaOH solution was added to the substrate at a
126liquid to solid ratio of 10 mL/g in a bottle, and mixed overnight on an
127orbital shaker. The undissolved fraction was discarded; the
128supernatant solution pH was adjusted to within 1 to 2 with 6 N HCl, and
129equilibrated overnight. After the precipitate was washed using water,
130dried at 75 °C, and weighted, it was ready to be used for Step 2. As an
131alternative pretreatment method, acid was used to remove mineral
132solids. 1.0 N HCl solution was added at a liquid to solid ratio of 10
133mL/g, mixed in a bottle on an orbital shaker overnight, decanted,
134rinsed with deionized water, and oven-dried for the next step. For the
135non-pretreatment approach, dry raw materials were directly used. In
136Step 2, the treated or non-treated material was subjected to Soxlet
137extraction with a solvent:solid ratio of 15:1 mL/g. The solvent used was
138a mixture of benzene and methanol (3:1 volumetric ratio), at 60 °C for
139~72 hrs. The remaining solid phase was discarded; the solvent was
140evaporated away and condensed for later reuse; and the extracts were
141harvested for Step 3. The solvent-extracted fraction was lastly

142subjected to alkaline cleaning. This final step served to remove the
143highly hydrophobic fraction that is insoluble in alkaline (0.1 M NaOH)
144solution. The solution to solid ratio of 30 mL/g was mixed in a bottle
145and shaken overnight, then centrifuged to remove the residual solids.
146The remaining supernatant containing NBS was ready for use as the
147stock solution after determine its NBS concentration. Dry NBS can be
148obtained by adjusting the solution pH to 1-2 with 6 N HCl, equilibrating
149overnight, centrifuge to remove the supernatant, and oven drying to
150recover the precipitate.

151

152**NBS chemical composition and function group analyses.** The
153solid NBS and intermediate products in the extraction process were
154analyzed for their chemical composition (C, H, N, O, S%) and function
155groups. The CHNOS analyses were performed by ALS Environmental
156Micro-elemental Laboratory (Tucson, Arizona. [http://www.caslab.com/
157Tucson-Laboratory/](http://www.caslab.com/Tucson-Laboratory/)) using PerkinElmer 2400 CHNS/O Series II
158combustion analyzer. To determine ash content, thermo gravimetric
159analyses (TGA) was used (TA Instruments SDT-Q600). To determine
160molecular functional groups, FTIR spectra were obtained with a Thermo
161Nicolet iS50 spectrometer. ATR spectra were collected with a MCTA
162detector; resolution of 2 cm⁻¹, 64 scans per sample, over the range of
163400 - 4000 cm⁻¹.

164

165**Air-water and scCO₂-water interfacial tension measurements.**

166The interfacial tensions (IFT) at air-NBS solution interfaces were
167measured using the Du Nouy ring method (K11, Kruss.com) under
168ambient conditions (23 °C, atmospheric pressure). For measuring
169scCO₂-NBS solution IFT, the pendant drop method was performed at 12
170MPa and 45°C. A high-pressure chamber with two transparent windows
171allows illumination and imaging of a fluid droplet formed and
172equilibrated within scCO₂¹². The chamber was instrumented with a

173pressure transducer, a thermocouple, and a movable needle used to
174inject the liquid droplet. Two high-pressure syringe pumps (Teledyne
175ISCO, 500D/65D) were used to control pressure and deliver scCO₂ and
176aqueous solution. Both scCO₂ and water are contained in the chamber
177to maintain mutual solubility equilibrium, after which a NBS solution
178droplet was introduced into the scCO₂ phase. Evolution of the shape of
179the droplet was monitored using high-resolution time-lapse
180photography. Because the shape of a droplet changes with time, only
181equilibrium images of droplets (5 minutes to 2 hours) were used for
182generating the IFT data. For each reported IFT value, at least 3 droplets
183were measured, with at least 5 images analyzed per droplet.

184

185**NBS stabilized foam generation.** We first used a simple method to
186generate air-in-water foam for evaluating the foam generation
187capabilities of all the NBS samples, and to identify optimal conditions
188(NBS concentrations, pH and ionic strength) for generating scCO₂-in
189water foams (Figure 2). In generating air-in-water foams, 2 mL of NBS
190solution was put in a small glass vial, sealed with a lid, and vigorously
191shaken for 1 minute. The height of the foam in the jar was recorded
192over time. We then selected the most promising set of parameters
193from the air-foam testing to generate scCO₂-foams using our
194laboratory-built foam generator and rheometer (Figure 2).

195 The foam generator consists of a stainless steel column (1.0 cm
196ID and 30 cm long) packed with sand (Unimin sand, 106 to 212 μm,
197permeability = 4.4×10^{-12} m², porosity ~0.38, pore volume 1.45 mL).
198Two high-pressure pumps (Teledyne, ISCO D-Series syringe pumps)
199were separately filled with one of the two fluids, NBS aqueous solution
200and scCO₂. With the two syringe pumps operated in parallel, the two
201fluids were co-injected into the sand column under selected volumetric
202flow ratios of 1:4 to 1:9, and combined flow rates ranging from 6 to 36
203mL per minute, while the downstream backpressure (varied between

204~8.5 and ~11 MPa) was controlled with a third ISCO pump. The
205rheometer (viscometer) was a capillary tube (stainless steel, 760 μm
206ID, 3.3 m long, coiled into a helix with a 0.17 m diameter), located
207immediately downstream of the sand column. Two pressure
208transducers at the ends of the coil allowed measurements of pressure
209drops and effective viscosities during flow. Prior to the foam tests, the
210rheometer was calibrated by pumping water at steady flow rates and
211correlating the measured pressure differential acting across the coiled
212capillary with the known viscosity water for the given temperature and
213average total pressure. These calibration measurements were found to
214be in good agreement with predictions for viscous flow in coiled
215tubes¹³. The pressure drops across the capillary tube measured during
216foam flow were then used to calculate apparent viscosities. The main
217components for the experimental system were kept within an insulated
218enclosure with temperature controlled at $45 \pm 1^\circ\text{C}$. The morphology of
219foams was visually monitored through the viewing window of a
220horizontally oriented Jerguson high pressure gage (Series 40, rated to
22134 MPa at 38°C), located downstream of the rheometer. Microscope
222images of finer scale foam morphology were obtained by diverting
223effluents into a glass micromodel (Micronit Microfluidics) ²¹, mounted
224on an inverted microscope (Zeiss, Observer Z1.m, with AxioCam MRc5
225CCD camera). Pressures ranging from 8.5 to 11 MPa were used for the
226foam tests, with the majority conducted in the 8.5 to 9.0 MPa range in
227order to remain within the 10.0 MPa pressure limit of the micromodel.

228

229

230

231

232 **Figure 1.** Photographs of raw materials (humus) tested for NBS
 233 extraction. The upper panel photographs show samples as received
 234 from different sources. The magnified images (lower panels) show
 235 morphology of remnant biological structure (sample FLP). The
 236 photograph with a loader and stockpile provides a snapshot of the field
 237 recovery of the raw material (photo with permission from Leonardite
 238 Products, LLC, Williston, ND).

239

240**Figure 2.** Schematic diagram of foam generator and rheometer for
 241supercritical fluid foams. The foam can be studied visually through the
 242window of the high-pressure viewing chamber and microscope at the
 243downstream of the viscometer.

244

245

246**RESULTS AND DISCUSSIONS**

247**NBS extraction and yields.** Photographs of four humus samples
 248used in this study are shown in Figure 1 with the magnified images
 249(bottom panel) showing remnants of degraded organic matter. The
 250NBS extraction yields from these humus samples are summarized in
 251Table 1, based on dry weights of raw humus. The product of alkaline-
 252pretreatment is called humic acid (HA). Because HA is a commonly
 253recognized organic matter fraction of soils, we also reported the

254extraction yields of HA, and NBS yields relative to HA. The yielded HA
255vary substantially, $58 \pm 9\%$. The solvent-extracted fraction accounts for
256 $35.8 \pm 1.7\%$ of HA, and the NBS yields accounts $30.0 \pm 2.8\%$ of the HA,
257and $17.3 \pm 2.6\%$ of the raw humus. These are average values obtained
258from the four raw humus samples tested shown in Table 1. The most
259important information here is that a large percentage ($\sim 17\%$) of the
260natural humus is extractable surfactant. It is also important to know
261that the NBS yields accounts for $30.0 \pm 2.8\%$ of HA, consistently from
262samples of different origins. The cost of NBS will largely associate with
263the extraction process instead of raw material, therefore high HA
264content should be considered as a criterion in selecting humus as the
265starting material. The final alkaline-cleaning step removed a small
266highly hydrophobic fraction ($\sim 6\%$ of HA) that does not dissolve in
267alkaline solution. The pretreatment of acid-wash resulted no significant
268but slightly (up to 2%) higher yields. Because the acid-pretreatment
269(omitting first obtaining HA) leaves a larger unwanted fraction to Step
2702, we decided not continue the acid-pretreatment approach. We also
271tested direct solvent-extraction without pretreatment. The results
272showed substantial reduced yields and increased extraction time, with
273one example presented at the last row of Table 1. Further studies on
274NBS extraction are necessary to optimize yields and quality. Many
275factors affect production yields and functions of the NBS, including
276extraction procedures and solvent selection. Today advanced
277separation technologies are widely used in industries ¹⁴, and a wealth
278of literature exists on methods development for shortening extraction
279time, reducing solvent usage, and simplifying procedures, including
280extraction under elevated pressure and temperature¹⁵, microwave-
281assisted, ultrasound-assisted, and supercritical CO₂ extractions¹⁶.

282 It should be noted that no further filtration or refinement of the
283NBS was performed for removal of colloids and nanoparticles likely
284present in the final extracts. Such separation would add to the cost of

285NBS extraction. Moreover, the presence of nanoparticles in the NBS
286may enhance the stability of CO₂-water interfaces, as demonstrated in
287other recent studies.

288

Table 1. NBS extraction yields (relative to dry raw humus and HA).

Sample ID	Sample Origin	¹ HA % from humus	² Solvent ext. % from HA	NBS % from HA	NBS % from humus
NDL	North Dakota (Leonardite Products, LLC, Williston, ND)	62.8	36.8	32.6	20.5
FLP	Florida (Organic Products Co. Orlando, FL)	43.3	37.4	30.7	13.3
ADL	Aldrich (Cat. # H16752)	68	33	25.2	17.1
IHSSP	IHSS (Cat. # 2BS103P)	57.6	36.1	31.4	18.1
IHSSP	IHSS (Cat. # 2BS103P)	no-pretreatment	NA	NA	11.6

¹Alkaline-pretreatment resulted humic acid (HA).

²Solvent extracts from HA.

Chemical composition and functional group characteristics. The C, H, N, O, S % composition data are normalized by assuming that the sum of C, H, N, S, O, moisture, and ash = 100%; and that O % = 100% - sum of [CHNS, moisture, ash] (**Table 2**). The data include examples from two complete sets of intermediate and final products including HA from alkaline-pretreatment, the discarded solvent-extraction fraction, the retained solvent-extraction fraction, alkaline-cleaning discarded fraction, and NBS. In addition, the compositions of another two NBS fractions and ash contents from TGA are presented for comparison (lower section of Table 2). Although there is considerable variability, the discarded solvent-extraction fraction had more hydrophilic components that contain more N and O groups from HA. The alkaline-cleaning discarded hydrophobic non-polar aliphatic groups containing higher C-H. The final NBS contain 53.1 ± 6.5% C, 4.4 ± 0.7 H%, 30.8 ± 1.4% O (in COOH and OH), and high C and H in phenolic rings.

The FTIR spectra from all extraction steps for NDL as an example

are shown in Figure 3a. The spectra of NBS extracted from all four humus samples are presented in Figure 3b. The broad band in the vicinity of 3300 cm^{-1} is attributed to O-H and N-H stretching. The peaks at 2920 and 2850 cm^{-1} , and 1450 cm^{-1} represent C-H stretch of aliphatic groups. The clear peaks 1720 and 1610 cm^{-1} are mostly contributed by aromatic C, carbonyl groups in ketones, aldehydes, carboxylic acids, and their functional derivatives. The peak near 1225 cm^{-1} may be the contributions of C-O and OH of COOH, C-O of aryl ethers and phenols¹⁷. In Figure 3a, the solvent-extraction discarded fraction (green spectrum) contains more hydrophilic (3300 cm^{-1}) groups, and the solvent-kept fraction (purple spectrum) contains relatively more amphiphilic C. The alkaline-cleaning step resulted in removal of a significant fraction of insoluble aliphatic C-H, as shown in blue spectrum with strong aliphatic bands at 2920 and 2850 cm^{-1} , as well as a distinct peak at 1450 cm^{-1} . These spectral trends are consistent with the chemical composition data in Table 2; showing that the solvent-extraction removed fractions higher in N and O, and that the alkaline-cleaning removed more C and H, and less O and N relative to the NBS fraction. It is important to note that different source material types (peat or leonardite) and geographic locations of the source humus do not result in significant differences in the overall chemical compositions and function group chemistry of their extracted NBS (Table 2 and Figure 3b), although variation in some detailed features is evident.

335

Table 2. Chemical compositions of NBS and their intermediate products*

Sample	C%	H%	N%	O%	S%	H ₂ O%	Ash%	C:N	C:H	C:O
NDL-pret-HA	51.5	4.7	2.9	31.9	0.3	5.5	3.5	17.7	10.9	1.6
NDL-solv-disc	57.0	5.2	2.8	28.5	0.3	4.7	1.8	20.1	11.0	2.0
NDL-solv-kept	53.6	5.1	2.7	26.9	0.3	6.2	5.5	19.9	10.4	2.0
NDL-clean-disc	66.4	8.2	1.2	16.6	0.1	2.5	5.1	54.8	8.1	4.0
NDL-NBS	58.0	5.3	2.4	29.6	0.3	4.7	0.1	24.1	11.0	2.0
FLP-pret-HA	55.4	4.2	1.6	31.7	0.2	3.6	3.5	35.8	13.1	1.8
FLP-solv-disc	55.2	3.9	1.6	32.6	0.2	3.7	3.1	34.1	14.3	1.7
FLP-solv-kept	57.6	5.1	1.1	29.3	0.2	4.2	2.8	52.4	11.4	2.0
FLP-clean-disc	70.1	8.2	0.7	17.7	0.1	3.3	0.0	97.4	8.5	4.0
FLP-NBS	57.0	4.9	1.1	29.7	0.2	5.4	1.9	51.3	11.6	1.9
IHSSP-NBS	55.7	4.1	1.3	33.0	0.6	5.9	0.0	42.9	13.6	1.7
ADL-NBS	41.9	3.4	0.9	30.7	0.5	5.5	17.6	48.7	12.2	1.4
FLP-NBS	57.0	4.9	1.1	29.7	0.2	5.4	1.9	51.3	11.6	1.9
NDL-NBS	58.0	5.3	2.4	29.6	0.3	4.7	0.1	24.1	11.0	2.0

339*Assuming the sum of C, H, N, S, O, moisture, and ash = 100%; and O
340% = 100% - sum of CHNS-moisture-ash. HA= humic acid; solv-disc =
341discarded fraction from solvent extraction; solv-kept = solvent
342extracted fraction; clean-disc = discarded fraction, non-dissolvable in
343alkaline solution; NBS = solvent extracted and alkaline solution
344dissolvable fraction.

345

346

347

348 **Figure 3.** FTIR spectra of intermediate and final extraction products.

349 **(a)** A complete set of spectra of intermediate and final products from
 350 NDL raw humus, including HA, solvent-extraction discarded, solvent-
 351 extraction kept, alkaline-cleaning discarded and the NBS. **(b)** Spectra
 352 of NBS extracted from four humus samples of different origins.

353

354 **NBS effects on air-water and scCO₂-water interfacial tensions.**

355 The measured interfacial tension (IFT) values of air-NBS solutions
356 under varying NBS concentrations are presented in Figure 4. The
357 measurements for the four NBS samples of different origins show that
358 IFT values rapidly decrease as NBS concentration increases within the
359 lower concentration range, $\text{NBS} < \sim 0.2$ mass %, and that IFT still
360 continues to decrease with concentration afterwards. Different from
361 synthetic surfactants, there is no clear critical micelle concentration
362 (CMC) found for the various NBS samples. The extent of decreased IFT
363 values is similar to those achieved with synthetic surfactants. For
364 example, at 25 °C, Enordet AOS 1416 reaches an IFT about 32 mN/m,
365 and Chaser SD1000 reaches an IFT of 47-40 mN/m at their micelle
366 concentrations¹⁸. Although there are clear differences among the four
367 NBS samples, in-depth studies of these samples are beyond the scope
368 of this paper. It is worth noting that the greatest reduction in IFT occurs
369 under alkaline conditions ($\text{pH} \geq 9.0$) The surface activity of NBS has a
370 relatively high tolerance to salinity, decreasing as salinity increases to
371 ≥ 1.0 M (NaCl).

372 Before measuring IFT between scCO₂ and NBS solutions, the
373 integrity of the high-pressure IFT measurement apparatus and
374 procedure were first tested through measuring the IFT between air and
375 pure water. Our measured air-pure water IFT at 22.5 °C was 72.3
376 mN/m, in good agreement with the value of 72.4 mN/m obtained with a
377 regression relation from a standard reference¹⁹. Another test was done
378 on the scCO₂-pure water IFT, where our measurement at 12.0 MPa and
379 45 °C yielded 24.2 mN/m, compared with 22 mN/m interpolated from
380 measurements at slightly different P-T conditions²⁰. Figure 5a shows an
381 example image obtained during the IFT measurements: a NBS-solution
382 droplet suspended within scCO₂ in the high-pressure chamber. The IFT
383 value was calculated based on the curvature of the droplet at the
384 equilibrium state. For each data point triplicate measurements (3

385 droplets) were conducted. NBS reduced IFT of scCO₂-NBS solutions
 386 down to 11.2 and 8.7 mN/m for the FLP-NBS at the NBS concentrations
 387 0.5% and 1.5%, respectively, respectively (Figure 5a). The data of
 388 NDL-1 and NDL-2 are from the alkaline- and acid-pretreated
 389 procedures, respectively. The different origins of the raw humus from
 390 which the NBS was extracted had relatively small influence on the
 391 extent of the IFT reduction (Figure 5b).

392

393

394 **Figure 4.** Measured air-NBS solution interfacial tension (IFT). All
 395 solutions contained 0.1 M NaCl and pH 6.5. The measurements were
 396 conducted at 22.5 ± 0.5 °C.

397

398

399**Figure 5.** Measuring interfacial tensions between scCO₂ and NBS
400solutions. (a) Example image of NBS solution droplet suspended within
401scCO₂ at 12.0 MPa and 45°C. Each IFT value was calculated from an
402image at the equilibrium state. (b) IFT values at NBS = 0.5g/L, pH 6.5,
403and 0.1 M NaCl for NBS samples of different origins. The NDL-1 and
404NDL-2 samples are from the alkaline- and acid-pretreated procedures,
405respectively.

406

407Generating NBS foams. A simple air-in-water foam method was first
408used for screening of NBS foaming ability and identifying foaming
409conditions for the scCO₂-foam experiment. Aqueous solutions were
410prepared with NBS of different origins, concentrations, pH and ionic
411strength. The photographs in Figure 6 show examples of NBS stabilized
412air-in-water foams generated by vigorously shaking sealed vials
413containing small amounts of NBS solution for 1 minute under ambient
414conditions. The NBS extracted from different original source materials
415all showed efficient foaming ability (Figure 6a), with no
416significant/systematic differences observed for foam height and
417duration. Note that the sample “Minnesota” (Peat Inc., Elk River, MN) in
418the photograph was not discussed in other sections because data are
419incomplete for this sample. Using this method, we determined that ~
4200.5% is the optimal NBS concentration (being both low and efficient).
421Increased NBS concentrations yielded longer lasting foams, but did not
422significantly increase the foam height. Decreased NBS concentration
423(down to 0.1%) resulted in significantly reduced foam height and
424duration. For the ionic strength effect, no significant differences were
425observed between 0.1 and 0.5 M, but NaCl concentrations higher than
4261.0 M reduced foam height and stability. We observed reasonable
427foaming ability over a wide range of pH from 3 to 9. While these tests
428provide information for screening stability ranges, more quantitative
429studies of the aforementioned parameters will be needed for
430developing applications suitable for specific environmental conditions.
431

432

433 **Figure 6.** NBS air-in-water foams generated by shaking sealed 20 mL
 434 vials containing 2 ml NBS solution (remainder of the vial volume filled
 435 with air under atmospheric pressure. **(a)** Different NBS origins showed
 436 no significant differences in the resulting foam height. **(b)** The pH
 437 effect (using FLP-NBS), showing good pH tolerance. The left-most vial
 438 shows the NBS solution before shaking.

439

440 The FLP-NBS was used to generate scCO₂-in-water foams
 441 (although the air-in-water foam tests, Fig. 6a, suggested that the other
 442 NBS may behave similarly). From the generation of air-water foams, an
 443 NBS concentration of about 0.5% appeared optimal. Therefore, we
 444 selected three NBS concentrations to test: 0.1, 0.5, and 1.0% for the
 445 scCO₂-foam experiment. For foam quality, we targeted 80% to 83%
 446 CO₂, and found this range to be readily achievable. For generating and
 447 characterizing the scCO₂-water foams, the scCO₂ and NBS-solutions

448were co-injected into the sand-packed column, after which the foam
449passed through the capillary tube viscometer (recording $\Delta P = P_3 - P_4$),
450and finally into the viewing chamber where the images of foam
451morphology were recorded (Figure 2). Apparent viscosities obtained
452with scCO₂ contents ranging from 80 to 83 % by volume, under
453different NBS concentrations in the aqueous phase, and a range of
454shear rates are shown in Figure 7. The co-injection rates ranged from
4556 to 36 mL/min, with most rates ranging from 9 to 18 mL/min. The
456corresponding Darcy flow rates and residence times within the
457sandpack were 1.3×10^{-3} to 7.6×10^{-3} m/s, and 90 to 15 s, respectively.
458It should be noted that the associated shear rates in the capillary tube
459viscometer, ranging from 2,300 up to 13,900 s⁻¹, are very high. Given
460the typical shear-thinning behavior observed from these
461measurements (Figure 7), apparent viscosities under much lower shear
462rates of field injection processes are expected to be significantly higher
463than the value of 13 cP obtained at 2,300 s⁻¹. These tests collectively
464indicate that scCO₂-water foams are viable with 0.5 to 1.0 % NBS in the
465aqueous phase, and that the 0.1 % NBS concentration may be
466inadequate. More systematic experiments targeted to testing behavior
467at low shear rates are necessary to optimize the foam generation
468procedure and foam properties.

469

470 **Figure 7.** Apparent viscosities of scCO₂-water foams (80 to 83 % CO₂
 471 by volume) at 8.5 to 9.0 MPa, for different concentrations of NBS in
 472 the aqueous phase. Viscosities of scCO₂ and H₂O are included for
 473 comparison.

474

475 Representative images of scCO₂-water foams using different
 476 NBS concentrations are presented in Figure 8. Although the NBS
 477 concentration of 0.1%, did not support high apparent viscosities
 478 under the tested very high shear rates, fairly consistent foams were
 479 generated, albeit with some mm-sized bubbles (Fig. 8a). The
 480 microscopic image of the 0.5% NBS case (inserted image in Fig. 8b)
 481 shows scCO₂ droplet sizes up to about 20 μm. When the NBS
 482 concentration was increased to 1.0% (Fig. 8c), the foam appeared
 483 mist-like. Example videos of foam flow through the viewing chamber
 484 are provided in the Supplemental Information.

485

486

487**Figure 8.** NBS generated scCO_2 -in-water foams with 0.8 foam
488quality, and varied NBS concentrations (0.1, 0.5, and 1.0 %) and
489constant ionic strength 0.58% NaCl in the aqueous phase. No
490additional chemicals and additives were applied. The width of the
491viewing window is 15 mm.

492

493SUMMARY

494To evaluate the economic feasibility of NBS for industrial-scale
495subsurface engineering applications, the cost of NBS relative to
496synthetic surfactants currently used is a critical factor that needs
497further research. Although it is premature to make reliable production
498cost projections, the NBS are abundantly contained in humus deposits
499that are inexpensive and easily obtained. The cost of raw humus
500materials is only ~\$25 per ton (not include the transportation). The
501laboratory bench scale extractions yielded an average ~17% NBS
502relative to the raw humus. The four common chemicals needed in

503extraction include sodium hydroxide and hydrochloric acid (non-
504reusable), and benzene and methanol (recycled), and no costly
505synthesis and purification procedures are involved. Differences in
506origins of the humus appear to impart no major differences in the
507chemical composition, structure, and function of the extracted NBS.
508Thus NBS appears to be potentially economically competitive. Our data
509show that NBS is effective for reducing interfacial tensions and for
510generating and stabilizing high quality air- and scCO₂-foams, indicating
511that it could be suitable for generating other types of foams and
512emulsions as well. Lastly, the benign nature of NBS will be an asset in
513reducing operational costs and environmental impacts.

514

515**ACKNOWLEDGEMENTS**

516This material is based upon work supported by (1) the Laboratory
517Directed Research and Development program (LDRD) of the Lawrence
518Berkeley National Laboratory (LBNL), and (2) the U.S. Department of
519Energy, Office of Fossil Energy, Office of Natural Gas and Petroleum
520Technology, through the National Energy Technology Laboratory
521(NETL), under Award Number DE-AC02-05CH11231 and FWP-
522ESD14085. Project management by Stephen Henry (NETL) is gratefully
523acknowledged. We thank the anonymous reviewers for their helpful
524comments.

525

526**References**

5271. (a) Gupta, D. V. S.; Bobier, D. M., The history and success of
528liquid CO₂ and CO₂/N₂ fracturing system. In *SPE Gas Technology*
529*Symposium*, Society of Petroleum Engineers: Calgary, Alberta, Canada,
5301998; p SPE 40016; (b) Wanniarachchi, W. A. M.; Ranjith, P. G.; Perera,
531M. S. A., Shale gas fracturing using foam-based fracturing fluid: a
532review. *Environ Earth Sci* **2017**, 76:91; (c) Liu, H.; Wang, F.; Zhang, J.;
533Meng, S. W.; Duan, Y. W., Fracturing with carbon dioxide: Application
534status and development trend. *Petrol Explor Dev* **2014**, 41 (4), 513-
535519.

5362. Enick, R. M.; Olsen, D. K. *Mobility and conformance control for*
537*carbon dioxide enhance oil recovery (CO₂-EOR) via thickeners, foams,*
538*and gels- A detailed literature review of 40 years of research*; National
539Energy Technology Laboratory: 2012; p 241.

5403. (a) Heller, J. P.; Dandge, D. K.; Card, R. J.; Donaruma, L. G. Direct
541Thickeners for Mobility Control of CO₂ Floods *SPE* [Online], 1985, p.
542679-686. <https://www.onepetro.org/journal-paper/SPE-11789-PA>; (b)
543Lee, J.; Dhuwe, A.; Cummings, S. D.; Beckman, E. J.; Enick, R. M.;
544Doherty, M.; O'Brien, M.; Perry, R.; Soong, Y.; Fazio, J.; McClendon, T. R.
545Polymeric and Small Molecule Thickeners for CO₂, Ethane, Propane,
546and Butane for Improved Mobility Control *SPE* [Online], 2016, p. 21.
547<https://www.onepetro.org/conference-paper/SPE-179587-MS>; (c)
548Trickett, K.; Xing, D. Z.; Enick, R.; Eastoe, J.; Hollamby, M. J.; Mutch, K.
549J.; Rogers, S. E.; Heenan, R. K.; Steytler, D. C., Rod-like micelles thicken
550CO₂. *Langmuir* **2010**, 26 (1), 83-88.

5514. (a) Nguyen, Q. P.; Alexandrov, A. V.; Zitha, P. L.; Currie, P. K.,
552Experimental and modeling studies on foam in porous media: A review.
553*SPE* **2000**, (SPE 58799); (b) Heller, J. P., CO₂ foams in enhanced oil
554recovery. In *Foam: Fundamentals and Applications in the Petroleum*
555*Industry*, Schramm, L., Ed. American Chemical Society: Washington,
556DC, 1994; pp 201-234; (c) Johnston, K. P.; da Rocha, S. R. P., Colloids in
557supercritical fluids over the last 20 years and future directions. *Journal*
558*of Supercritical Fluids* **2009**, 47 (3), 523-530; (d) Hirasaki, G. J.;
559Lawson, J. B., Mechanisms of foam flow in porous media: Apparent
560viscosity in smooth capillaries. *SPE Journal* **1985**, April 1985, 176-
561190; (e) Falls, A. H.; Musters, J. J.; Ratulowski, J., The apparent viscosity
562of foams in homogeneous bead packs. *SPE Reservoir Engineering*
563**1989**, May 1989, 155-164; (f) Kovscek, A. R.; Tang, G. Q.; Radke, C. J.,
564Verification of Roof snap off as a foam-generation mechanism in
565porous media at steady state. *Colloids and Surfaces A:*
566*Physicochemical Engineering Aspects* **2007**, 302, 251-260; (g) Chen,
567M.; Yortsos, Y. C.; Rossen, W. R., Pore-network study of the
568mechanisms of foam generation in porous media. *Physical Review E*
569**2006**, 73 (036304), 1-20.

5705. (a) Adkins, S. S.; Chen, X.; Nguyen, Q. P.; Sanders, A. W.;
571Johnston, K. P., Effect of branching on the interfacial properties of
572nonionic hydrocarbon surfactants at the air-water and carbon dioxide-
573water interfaces. *Journal of Colloid and Interface Science* **2010**, 346,
574455-463; (b) Adkins, S. S.; Chen, X.; Chan, I.; Torino, E.; Nguyen, Q. P.;
575Sanders, A. W.; Johnston, K. P., Morphology and stability of CO₂-in-
576water foams with nonionic hydrocarbon surfactants. *Langmuir* **2010**,
57726 (8), 5335-5348; (c) Da, C.; Xue, Z.; Worthen, A. J.; Qajar, A.; Huh, C.;
578Prodanovic, M.; Johnston, K. P., Viscosity and stability of dry CO₂ foams
579for improved oil recovery. In *SPE Improved Oil Recovery Conference*,
580Society of Petroleum Engineers: Tulsa, OK, 2016; Vol. SPE-179690-MS;
581(d) Johnston, K. P.; Alzobaidi, S.; Da, S.; Tran, V., High temperature

582ultradry carbon dioxide-in-water foam stabilized with viscoelastic
583surfactants. In *AIChE Annual Meeting*, AIChE: San Francisco, CA, 2016;
584(e) Xue, Z.; Worthen, A. J.; Da, C.; Qajar, A.; Ketchum, I. R.; Alzobaidi,
585S.; Huh, C.; Prodanovic, M.; Johnston, K. P., Ultradry carbon dioxide-in-
586water foams with viscoelastic aqueous phases. *Langmuir* **2016**, 32 (1),
58728-37.

5886. Kosaric, N.; Vardar-Sukan, F., *Biosurfactants : production and*
589*utilization--processes, technologies, and economics*. CRC Press: Boca
590Raton, 2015.

5917. Stevenson, F. J., *Humus chemistry : genesis, composition,*
592*reactions*. 2nd ed.; Wiley: New York, 1994; p xiii, 496 p.

5938. Sutton, R.; Sposito, G., Molecular structure in soil humic
594substances: The new view. *Environ. Sci. Technol.* **2005**, *in press*.

5959. (a) Hayase, K.; Tsubota, H., Sedimentary humic and fulvic acid as
596surface active substances. *Geochimica et Cosmochimica Acta* **1983**,
59747, 947-952; (b) Chilom, G.; Bruns, A. S.; Rice, J. A., Aggregation of
598humic acid in solution: Contributions of different fractions. *Organic*
599*Geochemistry* **2009**, 40, 455-460; (c) Aiken, G. R.; Mcknight, D. M.;
600Thorn, K. A.; Thurman, E. M., Isolation of Hydrophilic Organic-Acids
601from Water Using Nonionic Macroporous Resins. *Organic Geochemistry*
602**1992**, 18 (4), 567-573.

60310. (a) Tschapek, M.; Wasowski, C., The surface activity of humic
604acid. *Geochimica et Cosmochimica Acta* **1976**, 40, 1343-1345; (b) Von
605Wandruszka, R., The micellar model of humic acid: evidence from
606pyrene fluorescence measurements. *Soil Science* **1998**, 163, 921-930;
607(c) Tombácz, E., Colloidal properties of humic acids and spontaneous
608changes of their colloidal state under variable solution conditions. *Soil*
609*Science* **1999**, 164, 814-824; (d) Guetzloff, T. F.; Rice, J. A., Does humic
610acid form a micelle? *The Science of the Total Environment* **1994**, 152
611(31-35).

61211. Harwood, L. M.; Moody, C. J., *Experimental organic chemistry:*
613*Principles and Practice* Wiley-Blackwell: 1989.

61412. Jung, J. W.; Wan, J., Supercritical CO₂ and ionic strength effects on
615wettability of silica surfaces: Equilibrium contact angle measurements.
616*Energy and Fuels* **2012**, 26 (9), 6053-6059.

61713. Hart, J.; Ellenberger, J.; Hamersma, P. J., Single- and two-phase
618flow through helical coiled tubes. *Chem. Eng. Sci.* **1988**, 43 (4), 775-
619783.

62014. (a) Wu, Q.; Schleuss, U.; Blume, H. P., Investigation on Soil Lipid
621Extraction with Different Organic Solvents. *Angewandte* **1995**, 4
622(Januar), 347-350; (b) Jeannotte, R.; Hamel, C.; Jabaji, S.; Whalen, J. K.,
623Comparison of solvent mixtures for pressurized solvent extraction of
624soil fatty acid biomarkers. *Talanta* **2008**, 77 (1), 195-199.

62515. (a) Jansen, B.; Nierop, K. G. J.; Kotte, M. C.; de Voogt, P.;
626Verstraten, J. M., The applicability of accelerated solvent extraction
627(ASE) to extract lipid biomarkers from soils. *Applied Geochemistry*

628**2006**, 21 (6), 1006-1015; (b) Quenea, K.; Mathieu, J.; Derenne, S., Soil
629lipids from accelerated solvent extraction: Influence of temperature
630and solvent on extract composition. *Org Geochem* **2012**, 44, 45-52.
63116. (a) Wang, L. J.; Weller, C. L., Recent advances in extraction of
632nutraceuticals from plants. *Trends Food Sci Tech* **2006**, 17 (6), 300-
633312; (b) Marr, R.; Gamse, T., Use of supercritical fluids for different
634processes including new developments - a review. *Chem Eng Process*
635**2000**, 39 (1), 19-28; (c) Kaufmann, B.; Christen, P., Recent extraction
636techniques for natural products: Microwave-assisted extraction and
637pressurised solvent extraction. *Phytochem Analysis* **2002**, 13 (2), 105-
638113; (d) Luque-Garcia, J. L.; de Castro, L., Ultrasound: a powerful tool
639for leaching. *Trac-Trend Anal Chem* **2003**, 22 (1), 41-47.
64017. (a) Gostishcheva, M. V.; Belousov, M. V.; Yusubov, M. S.;
641Ismatova, R. R.; Dmitruk, S. E., Comparative IR spectral characteristics
642of humic acids from peats of different origin in the Tomsk area. *Pharm*
643*Chem J* **2009**, 43 (7), 418-421; (b) Senesi, N.; D'Orazio, V.; Ricca, G.,
644Humic acids in the first generation of EUROSOLS. *Geoderma* **2003**,
645116 (3-4), 325-344; (c) Tatzber, M.; Stemmer, M.; Splegel, H.;
646Katziberger, C.; Haberhauer, G.; Mentler, A.; Gerzabek, M. H., FTIR-
647spectroscopic characterization of humic acids and humin fractions
648obtained by advanced NaOH, Na₄P₂O₇, and Na₂CO₃ extraction
649procedures. *J Plant Nutr Soil Sc* **2007**, 170 (4), 522-529.
65018. Noll, L. A. *Ambient and high-temperature calorimetry of*
651*commercial surfactants*; National Institute for Petroleum and Energy
652Research: Bartlesville, OK, 1989; p 58.
65319. Vargaftik, N. B.; Volkov, B. N.; Voljak, L. D., International tables of
654the surface tension of water. *Journal of Physical and Chemical*
655*Reference Data* **1983**, 12 (3), 817-820.
65620. Bachu, S.; Bennion, D. B., Dependence of CO₂-brine interfacial
657tension on aquifer pressure, temperature and water salinity. *Energy*
658*Procedia* **2009**, 1, 3157-3164.
65921. (a) Kim, Y.; Wan, J.; Kneafsey, T. J.; Tokunaga, T. K., Dewetting of
660silica surfaces upon reactions with supercritical CO₂ and brine: Pore-
661scale studies in micromodels. *Environmental Science & Technology*
662**2012**, 46, 4228-4235; (b) Hu, R.; Wan, J. M.; Kim, Y.; Tokunaga, T. K.,
663Wettability effects on supercritical CO₂-brine immiscible displacement
664during drainage: Pore-scale observation and 3D simulation.
665*International Journal of Greenhouse Gas Control* **2017**, 60, 129-139.
666